

Optical Characteristics of Novel Bisazo Polymer for Rewritable Holographic Data Storage

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ABSTRACT

A novel photoresponsive polymer containing bisazo chromophores have been synthesized for comparative study with monoazo polymer. Since the bisazo structure has an extended π -conjugation electronic system, it is expected to have large intrinsic molecular birefringence that can realize large macroscopic photoinduced birefringence (Δn_{PI}) via photoinduced molecular re-orientation process of bisazo molecules. As a result, it was found that the large value of Δn_{PI} (0.17) could be obtained by using bisazo polymer at 514.5nm excitation with 1.0W/cm².

Keywords: Photoinduced Birefringence, Bisazo Chromophore, Monoazo Chromophore, Holographic Data Storage, Molecular Re-orientation

1. INTRODUCTION

Nowadays, two competing high-capacity new optical disc technologies, so called Blu-ray and HD-DVD, have been commercialized at the same time. These new optical disc systems allow us to record high definition (HD) digital TV broadcasts or movies. However, demands of recording capacity getting increase for huge information recording such as digital entertainment applications, security system, medical informatics. Still more, there is a physical problem of diffraction limit, because these new optical disc systems are based on a pit recording method on the surface of recording media. It is pointed out that a recording density of the optical disc based on the conventional method cannot exceed ~ 1 [Tb/inch²]. In order to overcome this density limitation, a novel architecture for recording technique is required. One of the most promising techniques is the method using optical near-field and another is holographic recording. The holographic recording can be breakthrough the recording density of current storage media since it can be record entire page of data through the full depth of the recording media.

So far, it has been intensively studied recording material as well as optical system for holographic recording [1]. Consequently, a high-performance material based on photopolymer for write-once usage has been extensively developed and the materials has been released that can satisfy many severe criteria for a practical application such as high photosensitivity, volume (or thickness) invariability, preservation stability, optical clarity, and mechanical strength [2-5].

On the other hand, materials for rewritable application are still at the initial stage of the progress. In our previous report, we have already developed azobenzene containing copolymers that exhibit extraordinarily large photoinduced birefringence Δn_{PI} (0.25) under 458nm excitation [6-7]. Thus, this material is considered as a promising candidate for rewritable holographic recording media. In connection with this previous research, it is required more systematic study for structural effect such as π -conjugation length of azo chromophore. Thus, we designed and synthesized a novel photoresponsive polymer containing monoazo and bisazo chromophores for comparative study. In this work, two examples of monoazo and bisazo structures with similar dipole moment were synthesized in order to compare and discuss about an influence of the π -conjugation length for its optical performance. Most important aspects for holographic recording application such as Δn_{PI} property have been investigated.

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2. PHOTOINDUCED BIREFRINGENCE OF BISAZOBENZENE MATERIALS

Optically induced molecular reorientation of azobenzene has been investigated for the past decades. The photo-triggered molecular reorientation of bisazobenzene could be generally explained as illustrated in figure 1 (a). In fact, the photoisomerization process of bisazobenzene is more intricate motion compared conventional monoazobenzene since the bisazobenzene consist double azo-bonding between three phenyl groups. However, the photoinduced molecular reorientation process is basically explained in a similar way. Here, we assume the case that an amorphous film containing azobenzene chromophores (monoazo or bisazo) is irradiated by linearly polarized beam. Azobenzene molecules are subjected *trans-cis* photoisomerization process when they absorb the light, but *cis*-form is not stable and easily relax back to the thermodynamically stable *trans*-form again. During this process, the molecular directions of the relaxed *trans* molecules need not coincide with those of the original state, since they have rotational freedom in three-dimensional space. Then, if we continue the beam excitation, *trans-cis-trans* isomerization cycles are iterated continuously. However, the molecules that lie in a direction perpendicular to the electric field of the incident excitation beam do not absorb the light because they don't have any transition dipole moment to the polarization direction of incident light. As a result, the molecules that align perpendicular to the electric field of the incident beam are excluded from the photoisomerization cycles, thus the population of such azobenzene molecules increases with the irradiation time. This whole process is called as photoinduced molecular reorientation (or photo-alignment) of azobenzene, and this causes a generation of macroscopic birefringence in the bulk as shown in figure 1 (b). The first application of photoinduced birefringence for holographic optical recording has been reported by Todorov *et al.* [8]. They have employed azobenzene doped PVA system. However, azobenzene attached side chain type polymers can exhibit superior performance than the doped system with respect to this phenomenon due to their optical properties, chemical and physical stability, and processability. Therefore, we have designed and synthesized new side chain type polymers consist of monoazo and bisazo chromophores. Then their optical performance was compared.

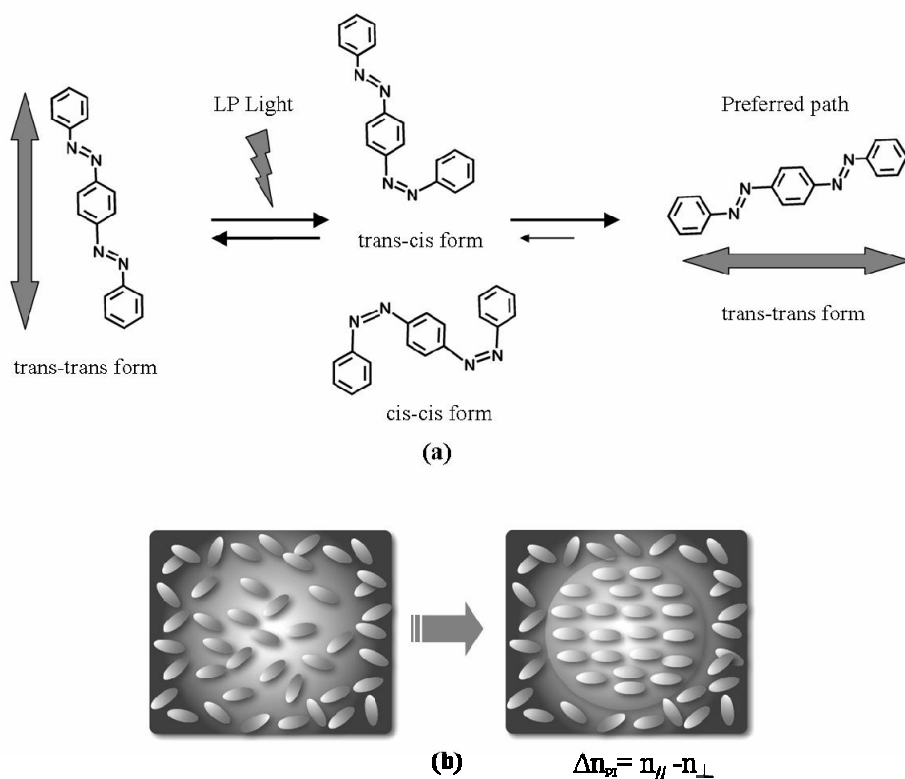


Figure 1. Schematic illustration of photo-triggered molecular re-orientation in bisazobenzene (a), photoinduced macroscopic birefringence (b); Inside of a bright circle indicates photo-irradiated area.

3. MATERIALS AND FILM PREPARATION

The monoazo polymer and the bisazo polymer were synthesized in order to compare the Δn_{PI} property, respectively. The cyanoazopyridine group of both polymers was introduced as photo-trigger with good optical response. The bisazo polymer was designed for large birefringence, high order parameter and good stability of re-oriented alignment. The monoazo compound was obtained by azo coupling reaction and then the spacer of two methylene unit was attached to the compound via Williamson reaction. After that, in order to radical polymerization, the methacrylate unit was introduced to above compound via simple esterification reaction. The polymer product was obtained by radical polymerization of the monomer initiated with AIBN. The bisazo polymer also obtained by above similar procedures with additional azo coupling reaction.

The chemical structures of the polymers are shown in figure 2. The synthetic procedure was slightly modified from previous report [6]. More detailed synthetic procedure will be published elsewhere.

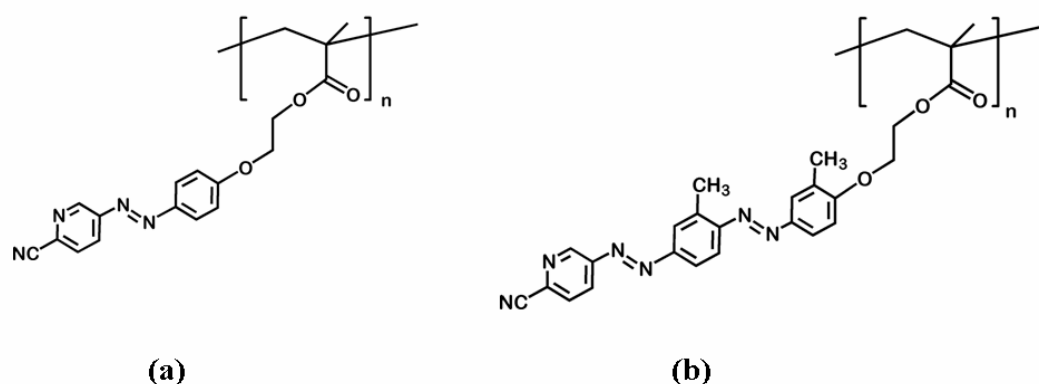


Figure 2. The chemical structures of monoazo polymer (a) and bisazo polymer (b).

The polymers were dissolved in DMF at a concentration of 2 wt% and filtered through a membrane with 0.2 μm pores. Then the solutions were spin coated onto a glass substrate at 700rpm for 30second in the dried nitrogen atmosphere. From our preliminary experiments, it was pointed out that the optical quality of the film strongly affects the absolute value of the Δn_{PI} . Therefore, we have paid great attention to the spin coating procedure in order to obtain homogeneous, smooth and non-scattering thin film. Finally, optically clear films (0.1~0.12 μm -thick) were obtained.

4. OPTICAL CHARACTERISTICS

The Δn_{PI} characteristics were evaluated by an optical setup shown in figure 3. Ar^+ laser (Coherent, $\lambda = 458, 488, 514.5\text{nm}$, beam diameter = 3mm and irradiance = $1\text{W}/\text{cm}^2$) and He-Ne laser (Melles Griot, $\lambda = 633\text{nm}$, beam diameter = 1mm and power = 3mW) were employed for excitation and probe beam, respectively.

Two beams were in collinear and incident normally on the sample film. The polarization conditions of both incident beams were controlled to linear polarization by a polarizer and half-wave plate, and the direction of the He-Ne beam was set to vertical and that of the Ar^+ beam was set to -45° with respect to the He-Ne beam. The change in polarization condition of transmitted He-Ne beam was monitored by measuring Stokes' parameters with a polarimeter (Thorlabs, PA510). Transmitted Ar^+ beam was stopped on the line with sharp cut filter before the polarimeter. The Δn_{PI} value was estimated by the observed Stokes' parameters and the film thickness.

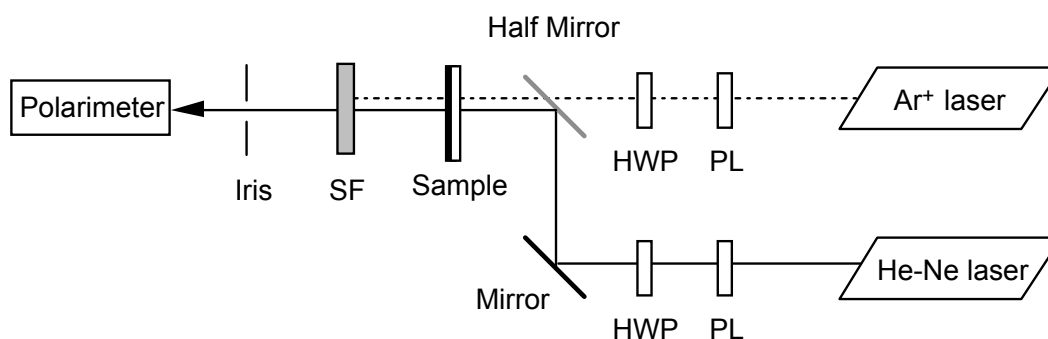


Figure 3. Schematic illustration of the optical setup for photoinduced birefringence (Δn_{PI}) measurement. PL = polarizer, HWP = half wave plate, SF = sharp cut filter.

5. RESULTS AND DISCUSSION

We designed the bisazo monomer (figure 4) with an extended π -conjugation for highly anisotropic structure. The methyl groups were substituted on 2-, and 2'-positions of bisazo monomer in order to prevent inter molecular aggregation. Also these substituents give a better solubility for organic solvents. The spacer length between chromophore and main chain is designed relatively short because the longer spacer brings about an increase of liquid crystallinity of the side chain and this causes a reduction of a phase transition temperature of the material, which is not appropriate to ensure a long-term stability of photoinduced molecular re-orientation. ^1H -NMR spectrum of bisazo monomer is given in figure 4.

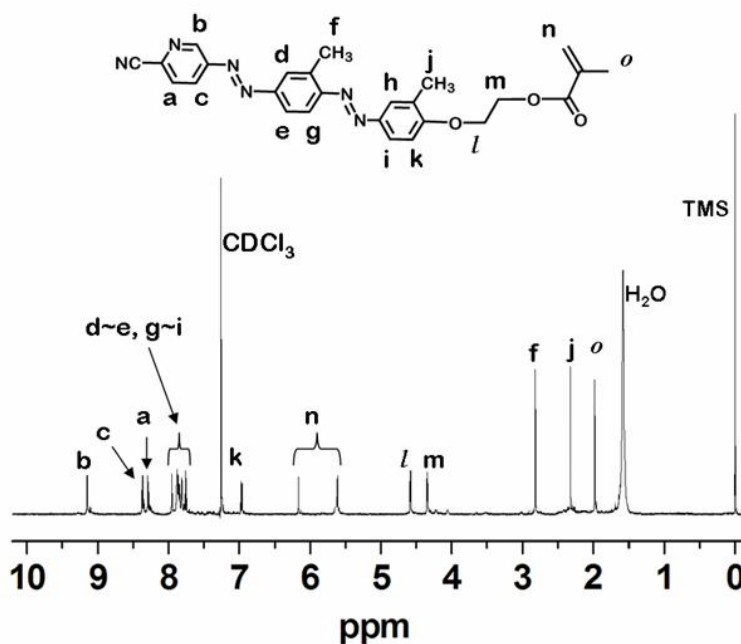


Figure 4. ^1H -NMR spectrum of bisazo monomer.

The UV/Vis spectra of the monoazo polymer and bisazo polymer were shown in figure 5. The maximum absorption peaks of the monoazo and bisazo polymer were observed at 371nm and 382nm, respectively. These main bands are attributed to π - π^* transition of both monoazo and bisazo chromophores. Tails of absorption band in the visible region continues up to 550nm and 620nm, respectively. So that the chromophores are able to absorb and respond to the excitation beam of 458, 488, 514.5 nm excitation beams. Also, both chromophore containing a weak electron donor (-OCH₂CH₂-) and strong electron acceptor (-CN) groups. Comparing to the absorption spectra, maximum absorption of bisazo polymer was shift to longer wavelength and much broad absorption band was observed. This is originated from a difference of π -conjugation length between monoazo and bisazo polymer.

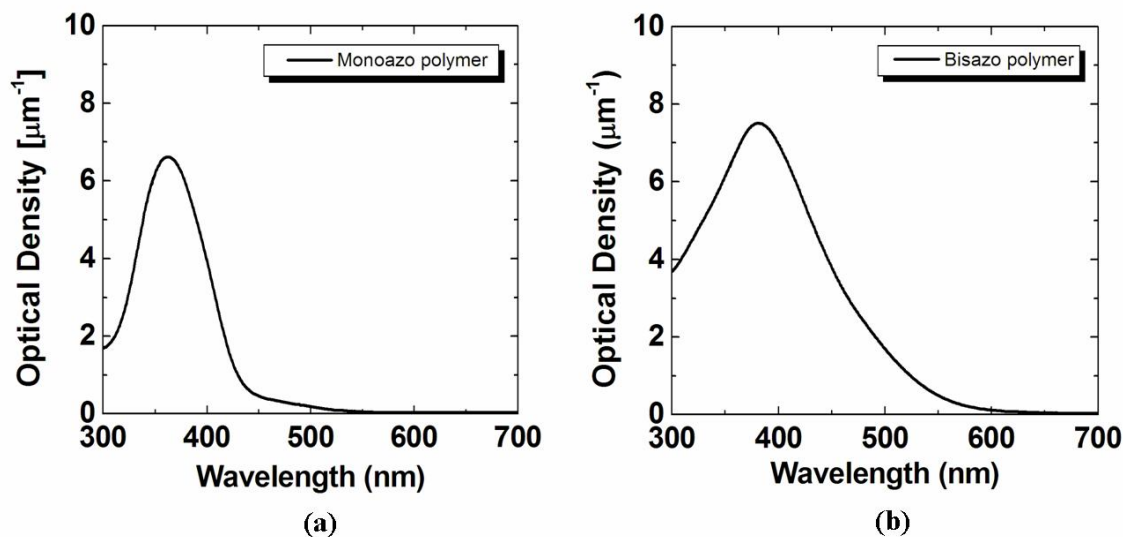
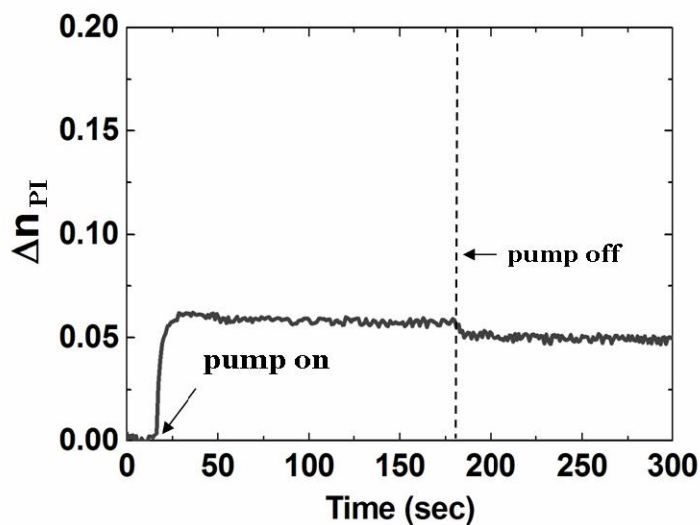


Figure 5. The UV/Vis absorption spectra of the monoazo polymer (a), and the bisazo polymer (b). The optical density was calibrated by each film thickness.

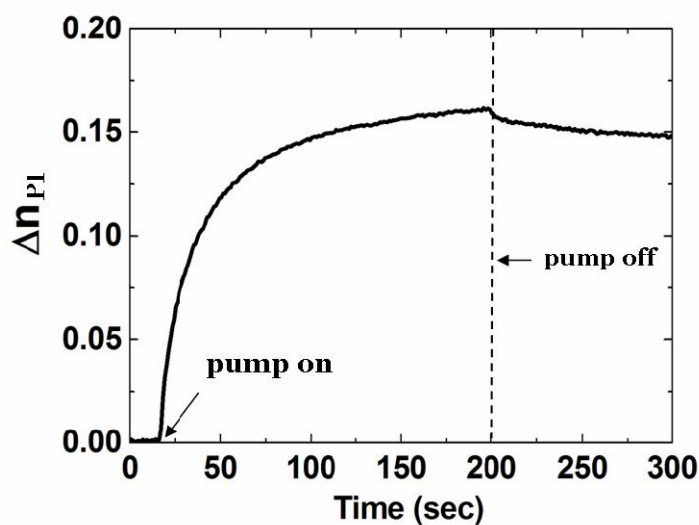
The dynamics of the Δn_{PI} of mono and bisazo polymers were shown in figure 6. At the initial state, macroscopic birefringence was not observed since the chromophores were in a random orientation. Then an anisotropic molecular alignment in the film was induced immediately under the pump beam excitation due to the photo-triggered molecular reorientation. As we expected, it was found that the bisazo polymer exhibit a large Δn_{PI} value of 0.161 under 488nm excitation with 1W/cm². This value is approximately three times larger than that of the monoazo polymer (Δn_{PI} =0.058) at the same condition. The values of intrinsic molecular birefringence were calculated by MOPAC with PM5 parameter as 0.405 and 0.746 for monoazo and bisazo chromophores, respectively. Thus, the observed values of macroscopic photoinduced birefringence suggest that the monoazo and the bisazo chromophores were aligned with the order parameter of 0.143 and 0.216, respectively. One of the reason to explain the fact, that photoinduced order parameter is bisazo chromophore is larger than that in monoazo chromophore, the bisazo chromophore is able to maintain the photo-triggered alignment due to a steric effect of highly anisotropic molecular shape. And one more possible reason is that the bisazo chromophore exhibits more effective *trans-cis-trans* photoisomerization, since it has stronger absorbance at the excitation wavelength (488nm).

In addition, if we define the response time as the elapsed time requiring for the Δn_{PI} value increment from 10% to 90% value, we can compare the initial response characteristics in more detail. The response times of the mono and the bisazo polymer were evaluated as 6 and 73 sec, respectively. As we indicated in chemical structure of the bisazo polymer, it includes highly anisotropic chromophore. In the condensed state as a solid film, such a bulky chromophre is not allowed to move and takes a long time to re-orient perpendicular to the incident beam polarization. Therefore, initial response time of bisazo polymer was obviously slower than monoazo polymer. However, this response time of the bisazo

polymer is not inferior to the other conventional azobenzene polymers. Still more, it should be emphasized that there was not any obvious relaxation after an excitation beam terminated. The saturated absolute value was still kept in 93% at 100~120s after the excitation beam terminated.



(a)



(b)

Figure 6. The dynamics of the Δn_{PI} in monoazo polymer (a), and bisazo polymer (b) as a function of the excitation times. The pump beam was turned on at 18sec and turned off at 180~200sec, Relaxation behavior was monitored for successive 100~120sec.

The wavelength dependence of the Δn_{PI} was measured on the bisazo polymer at 458, 488, and 514.5nm. The excitation irradiance was set to the constant of $1\text{W}/\text{cm}^2$ on this experiment. The optical densities of the bisazo polymer film at those three wavelengths are 3.36, 2.12, and 1.27, respectively. As a result, the tendencies of Δn_{PI} dynamics with different wavelength excitation were found to be similar and almost the same Δn_{PI} value were obtained (figure 7), even though the absorbance of the film was quite different at those three wavelengths. The highest Δn_{PI} value was 0.17 for 514.5 nm excitation. This might be explained from the viewpoint of light absorption in the film. In other word, it is better to choose the excitation wavelength to achieve an enough penetration depth of the excitation beam, otherwise the beam cannot illuminate whole the part of the film and just absorb at the close vicinity of the film surface. In addition, it might be expected to obtain higher Δn_{PI} value if we could employ a frequency doubled YAG laser (532nm) as a pump beam.

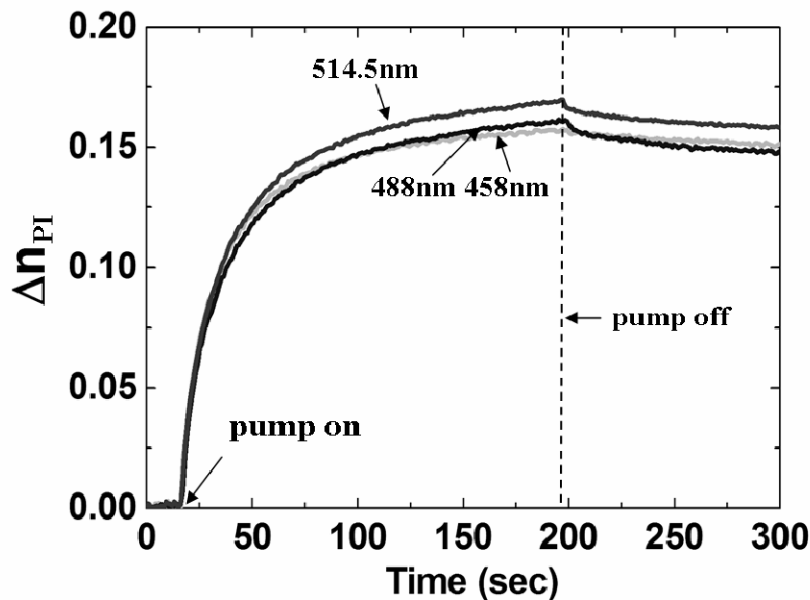


Figure 7. The wavelength dependence of the Δn_{PI} in bisazo polymer as a function of the excitation times. The pump beam was turned on at 18sec and turned off at 190sec, Relaxation behavior was monitored for successive 110sec.

5. CONCLUSION

In summary, we have developed new bisazo polymer, which can exhibited superior optical performance with respect to the Δn_{PI} , i.e., $\Delta n_{PI} = 0.17$ under the 514.5nm excitation with $1.0\text{ W}/\text{cm}^2$. This obtained Δn value of bisazo polymer is nearly triple value of monoazo polymer at the same condition. This result suggests that an adequate elongation of the π -conjugation system in azo chromophore brings about the enlargement of the molecular intrinsic birefringence and the stability of the photo-triggered alignment state. Even more, the order parameter of the photo-triggered aligned state was also increased in our system. Therefore, we believe that the results give a good direction to the further development of a high performance material for rewritable holographic recording.

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